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**Preliminary communication**

# THE MOLECULAR STRUCTURE OF A GERMENE $GeR_2$ ($R = CH(SiMe_3)_2$) BY GAS ELECTRON DIFFRACTION; SELF-CONSISTENT-FIELD MOLECULAR ORBITAL CALCULATIONS ON STANNENE, $SnH_2$, AND DISTANNENE, $Sn_2H_4$

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## Summary

$Ge[CH(SiMe_3)_2]_2$ is a V-shaped monomer in the gas phase at ca. 430 K, with Ge—C 204(2) pm and angle CGeC = 107(2)°; ab initio MO calculations on $Sn_2H_4$, with better than double $\zeta$ basis, indicate that (i) a non-planar *trans*-folded conformation is more stable than a planar structure by 26 kJ $mol^{-1}$, and (ii) the optimal angle between the Sn—Sn vector and an $SnH_2$ plane is 46°.

The Group IV metal(II) alkyls $(MR_2)_n$ ($M$ = Ge or Sn, $R = CH(SiMe_3)_2$) at present represent a unique class of compounds, which exist as monomers ($n = 1$, the carbene analogues) or dimers ($n = 2$, the alkene analogues) depending on phase. Points of interest for each of $MR_2$ and $M_2R_4$ include (i) the equilibrium geometry; (ii) M—C angles and CMC bond lengths and angles; (iii) trends as between M = C, (Si), Ge, and Sn; and (iv) for $MR_2$, comparisons with related $MX_2$ molecules. The present communication addresses these problems, and provides (a) experimental results on the gas phase structure of $GeR_2$ and (b) computational data on $SnH_2$ and $Sn_2H_4$ (as models for $SnR_2$ and $Sn_2R_4$).

The compounds $GeR_2$ and $SnR_2$ ($R = CH(SiMe_3)_2$) are monomeric in hydrocarbon solution and in the gas phase (by mass spectrometry or photoelectron spectroscopy) [1]. The molecular structure of gaseous $SnR_2$ (by gas electron dif-

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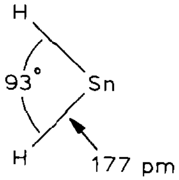
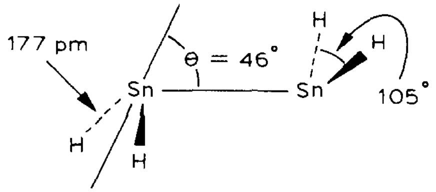


(I)



(II)

The optimal Sn—Sn bond distance in $Sn_2H_4$, 271 pm, is slightly shorter than the experimental value for $Sn_2R_4$, 276 pm [1]. The experimental CSnC angle in $SnR_2$ is 97° [2]; in $Sn_2R_4$ it has increased to 112° [1]. A similar difference is now found between the optimal HSnH angles in $SnH_2$ (93°) and $Sn_2H_4$ (105°). The larger angles in the alkyl derivatives may be due to steric factors.

The equilibrium conformation of $Sn_2H_4$ is *trans*-folded with $\theta$ 46°; the experimental values [6] for $\theta$ in $Ge_2R_4$ and $Sn_2R_4$ are 32 and 42°, respectively. The energy of the equilibrium conformation of $Sn_2H_4$ is 26 kJ $mol^{-1}$ below the optimum planar model (where Sn—Sn 255 pm). The stability of a *trans*-folded relative to a planar structure increases along the series $C_2H_4$, $Si_2H_4$, $Ge_2H_4$, and $Sn_2H_4$ (as was previously shown diagrammatically for the first three members [2]). In $Sn_2H_4$, $\theta$ is calculated to be only 6° larger than in $Ge_2H_4$, but stabilisation by *trans*-folding is 26 vs. 12 kJ $mol^{-1}$.

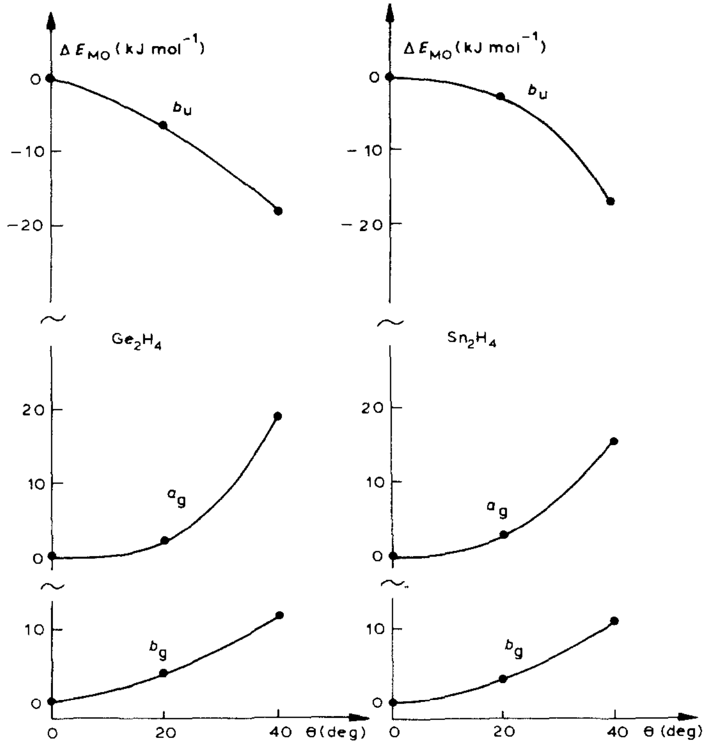


**Fig. 2.** Variation of energies of the three highest occupied molecular orbitals of $Ge_2H_4$ and $Sn_2H_4$ with the fold angle $\theta$.

fraction (GED)) is V-shaped, with Sn—C 224(1) pm and angle CSnC 96(1)° [2].

The electron diffraction pattern of $GeR_2$ was recorded with reservoir and nozzle temperatures of about 430 K corresponding to a vapour pressure of about 1 torr. Structure refinements were based on a model of $C_2$ symmetry defined by three bond distances (Ge—C, Si—C, and C—H), five valence angles, and three torsional angles. Least-squares refinements gave Ge—C 204(2) and Si—C(mean) 189(1) pm; angles CGeC 107(2)°, GeCSi 111(1)°, and SiCSi 113(1)°. The other structure parameters are unexceptional, Fig. 1.

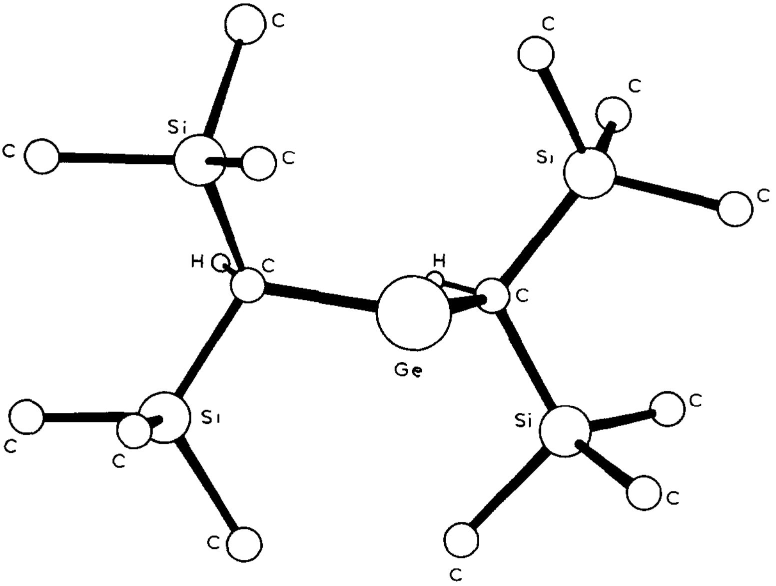


Fig. 1. Molecular structure of $Ge[CH(SiMe_3)_2]_2$, as determined by gas-phase electron diffraction.

The Ge—C bond distance is about 10 pm larger than in $GeMe_4$, 194.5(3) pm [3]. A similar $M^{II} \rightarrow M^{IV}$ SnC bond-shortening was noted in $SnR_2$ vs. $SnMe_4$ [2]. Surprisingly, the CGeC valence angle is now found to be ca. 10° larger than CSnC in $SnR_2$. Previously we noted (i) a similar, but somewhat less marked, monotonic decrease in the angle at M of the isoelectronic amides $M[N(SiMe_3)_2]_2$ (NMN 101(1.5) (M = Ge), 96 (M = Sn), or 91(2)° (M = Pb)), attributed to Bent's rule; and (ii) a similar $M^{IV}$—N → $M^{II}$—N bond-lengthening [4]. A further manifestation of Bent's rule is that $CM^{II}C > NM^{II}N > OM^{II}O$ (from X-ray data on $M(OAr)_2$, Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4) [5]; however, the large CGeC angle is probably due to steric effects.

Studies by X-ray crystallography show that $GeR_2$ [6] and $SnR_2$ [1] are dimeric in the solid phase. The $C_2MMC_2$ fragments are *trans*-folded, the angle between the M—M vectors and $MC_2$ plane being $\theta$ 32° (M = Ge) and 41° (M = Sn). Ab initio MO calculations on $Ge_2H_4$ [7] (see also refs. 2 and 8) have yielded *trans*-folded equilibrium structures with $\theta$ ranging from 34 to 40°.

We now report the results of similar calculations on $SnH_2$ and $Sn_2H_4$, with better than double-$\zeta$ basis [9]; the calculated equilibrium structures are summarised in I and II [10].

In Fig. 2 we show the variation of the orbital energies of the HOMO's of $Ge_2H_4$ and $Sn_2H_4$ as functions of $\theta$. In both molecules the energy of the $b_u$ (M—M $\pi$-bonding) orbital drops when $\theta$ is increased from zero. (The effect is due to mixing with the M—M $\sigma$-antibonding orbital.) The energy of the $a_g$ (M—M $\sigma$-bonding) orbital increases with $\theta$. The non-planar equilibrium structures of these molecules may thus be attributed to the "inertness" of the $b_u$ electrons. In the equilibrium conformation, these electrons constitute a delocalised lone-pair in metal-centred (*sp*)-hybrid orbitals; the stabilisation by $\pi$-bonding in the planar form does not apparently compensate for the $sp \rightarrow p$ promotion energy.

If $Ge_2H_4$ and $Sn_2H_4$ were *cis*-folded, mixing of the $b_u$ HOMO with the $\sigma$ antibonding orbital is forbidden by symmetry. The SCF energy is therefore found to increase with $\theta$, and internal rotation about the M—M bonds is restricted.

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